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Infrared and Raman Spectra of C_{60} and C_{70}
Solid Films at Room Temperature

by

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Infrared and Raman Spectra of C_{60} and C_{70} Solid Films at Room Temperature

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Abstract:

Infra-red and high resolution Raman spectroscopic probes of thin films of C_{60} and C_{70} are presented and discussed in terms of previous measurements, semi-empirical calculations and plausible molecular geometries.

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The development of simple methods for the gram scale synthesis of air stable hollow core all-carbon clusters (fullerenes)¹ has accessed a new class of solid materials whose properties are expected to hold many useful surprises. For example, preliminary studies on alkali doped C_{60} have shown resulting materials to be molecular superconductors with transition temperatures in the 18-30 K range². Pure fullerenes are presently being studied in applications ranging from lubrication³ to the nucleation of diamond thin films⁴. An understanding of the molecular level processes accessed in such studies requires structural determination, as well as sensitive and selective quantitative analysis. Both can be achieved via vibrational spectroscopy.

First FT-IR absorption^{1,5-7} and Raman measurements^{8,9} have established that room temperature solid films of C_{60} and C_{70} manifest characteristic vibrational spectra differing strongly from those of other carbon modifications. The high symmetry of the C_{60} truncated icosahedron (see figure 1) gives rise to only 4 IR and 10 Raman active modes¹⁰⁻¹². Their tentative assignment in IR and Raman measurements of C_{60} thin films has provided strong evidence for the proposed molecular structure⁹. Interestingly, the associated Raman depolarization ratios suggest effectively random molecular orientation at room temperature - consistent with a plastic r.t. phase inferred from solid state ^{13}C -NMR¹³. The supposed lower symmetry molecular structure of C_{70} ¹⁴ would be expected to lead to much more complicated vibrational spectra^{15,16} and in fact 21 Raman and 16 IR features have so far been reported for this cluster⁹.

In this letter we present Raman and IR measurements on C_{60} and C_{70} thin films. Raman data were obtained at significantly greater resolution (9x) than in previous studies. Results encompass a confirmation of C_{60} IR and Raman spectral assignment⁹ as well as the identification of multiple previously unresolved C_{70} vibrational features, which are compared to computational prediction. Detailed analysis of the underlying vibrational dynamics at various film temperatures is ongoing and will be reported elsewhere. This study is part of an investigation into the vibrational properties of carbon species involved in the nucleation and growth of diamond thin films⁴.

C_{60} and C_{70} were obtained from carbon soot, prepared by graphite evaporation in a helium atmosphere^{1,17}. Fullerenes were solvent extracted and chromatographically separated¹⁸. Purity of resulting C_{60} and C_{70} fractions was confirmed by electron impact mass spectroscopy (see below). Thin films were generated by subliming the respective purified solids under high vacuum onto Si(100) or KBr substrates. C_{60}/C_{70} were sublimed at 450/550° C, respectively. At lower evaporator temperatures, the substrate was kept shuttered. Raman spectra of fullerene films on silicon substrates were taken in air at room temperature in a backscattering geometry using either the 514 nm or 488 nm lines of an Ar⁺ laser (20 mW). No significant excitation frequency dependence was observed. Both polarized and unpolarized

spectra were obtained. Instrument resolution was 1 cm^{-1} with absolute error $\pm 1\text{ cm}^{-1}$. IR measurements were performed on KBr substrates using an N_2 -purged Mattson FTIR at 2 cm^{-1} resolution.

Unpolarized Raman spectra of C_{60} and C_{70} are shown in Figures 1a and 1b, respectively and compared to semi-empirical computation¹⁵. Tables I and II contain peak positions, intensities and symmetry assignments. Also listed are depolarization ratios for bands having sufficient signal-to-noise to yield meaningful numbers. Figures 2a and 2b show the corresponding IR absorption spectra again compared to calculation. IR spectral features are also listed in Tables I and II.

(i) C_{60} . IR and Raman spectra are in good agreement with previous work⁹. Using more recent semi-empirical calculations for $I_h\text{C}_{60}$ vibrational fundamentals¹², our data confirm the proposed spectral assignment, including 1100 and 1250 cm^{-1} features which had only been tentatively identified before. All IR active (4) and Raman active (10) modes are now clearly resolved. Among several additional (weaker) IR features, contaminant lines at 805 , 1257 , 1539 cm^{-1} (IR) are not tabulated⁹. Remaining minor tabulated features reflect combination bands or matrix effects.

(ii) C_{70} . The proposed D_{5h} structure (see figure 1) encompasses 31 IR and 53 Raman active modes. IR absorption studies have so far resolved 16 features⁹. We confirm 13 of these. At the higher resolution and sensitivities accessed, 21 previously identified Raman lines give way to a total of 33 features, some with discernible (and likely further separable!) shoulders. While similarities are apparent between experiment and D_{5h} semi-empirical prediction¹⁵ for both IR and Raman spectra, assignment must await: (i) more highly resolved measurements on thin films of $^{13}\text{C}_{70}$ and $^{12}\text{C}_{70}$ at various temperatures and (ii) calculations of Raman cross sections. In the interim, Table II gives tentative vibrational symmetry assignments for a number of lines based on calculations for the D_{5h} structure¹⁵.

The isolation of C_{70}O , $\text{C}_{76}/\text{C}_{78}$, C_{84} and C_{92} from fullerene preparations has recently been reported¹⁹. The underlying "statistical synthesis" from graphite likely forms traces of even larger all carbon clusters. Their isolation and mass spectral characterization is ongoing⁸. It is likely that such larger species will share with C_{60} and C_{70} the hollow core structural motif comprising 12 five fold rings (to achieve closure) supplemented by hexagons (20 in the case of C_{60}). Given enough carbon atoms, the vibrational spectra of large fullerenes should approach those of (perturbed) microcrystalline graphite²⁰. Systematic Raman studies of these systems may be of great interest in unraveling the size dependent transition from molecular vibrational to bulk phonon behaviour.

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Tables

I. C₆₀ IR and Raman line positions^a, relative intensities (unpolarized), Raman depolarization ratios and assignments.

Assignment	ν_{IR}	I_{IR}	ν_{RAMAN}	I_{RAMAN}	ρ^b
			267(S)	7	
H _g			273	15	.36
H _g			434	3	.47
			486(S)	3	
A _g			496	13.1	.07
F _{1u}	527	100			
F _{1u}	577	37			
H _g			710	4	.40
H _g			774	4	.46
H _g			1100	1	
F _{1u}	1183	23			
H _g			1250	1	
H _g			1426	13.1	.35
F _{1u}	1428	24			
			1464(S)	29.2	
A _g			1470	100	.08
H _g			1576	8.1	.39

^aPositions in wavenumbers. All features with signal to noise > 2 are listed (see figs. 1/2 and text). Typical relative intensity variations between measurements were $\pm 10\%$. Raman measurements were done on essentially pure C₆₀ and C₇₀ samples. The C₇₀ IR sample was slightly contaminated by C₆₀. ^bDepolarization ratios refer to $I_{\text{perpendicular}}/I_{\text{parallel}}$. Numbers are not tabulated for weak signals or incompletely resolved shoulders (s).

II. C₇₀ vibrational line positions, relative intensities, Raman depolarization ratios and tentative assignments^a.

Assignment (IR/Raman)	ν_{IR}	I_{IR}	ν_{RAMAN}	I_{RAMAN}	ρ
a_1'	458	16	224(S)	5	.24
			229	5	
			252(S)	24	
			260	31	
			400	7	
			413	17	
			436	3	
			457	10	
			508	4.3	
			521	5	
$/a_1'$	535	47	572	17	.12
	565	16			
	578	53			
	641	16			
$e_1'/?$	673	35	704	19	.4
			715	12	
e_2' or e_1''	795	19	740	16	.75
e_2' or e_1''			771	7	.7
e_1'			1053(S)	7	.29
a_1'			1063	26	
$a_2''/$	1133	13	1167	9	.25
$/a_1'$	1181	7	1187	69	
a_1'			1232	76	.2
e_2' or e_1''			1259	10	.62
e_2' or e_1''			1301	7	.5
			1316	12	
$/e_2'$ or e_1''	1320	7	1335	14	.54
			1371	24	.67
e_1'	1415	26	1439(S)	26	.23
$e_1'/$	1429	100		33	
a_1'	1460	6.9	1443(S)	71	
			1449	26	
			1461(S)	26	
			1463(S)	26	
a_1'			1471	52	.21
e_2' or e_1''			1515	22	.59
a_1'			1569	100	.29

^aSee table I footnotes.

Figure Captions

Figure 1. Unpolarized Raman spectra of purified films of C_{60} and C_{70} on Si(100) substrate - see text and Tables. Superimposed are the calculated Raman active modes [MNDO frequencies scaled to C_{60} measurement using $0.872x$]¹⁵ for both the C_{60} I_h structure and the postulated C_{70} D_{3h} structure.

Figure 2. FTIR spectra of purified films of C_{60} and C_{70} on KBr substrates. Also shown are the semi-empirical computational predictions of ref. 15 upon which we base the symmetry assignments in Tables I and II.

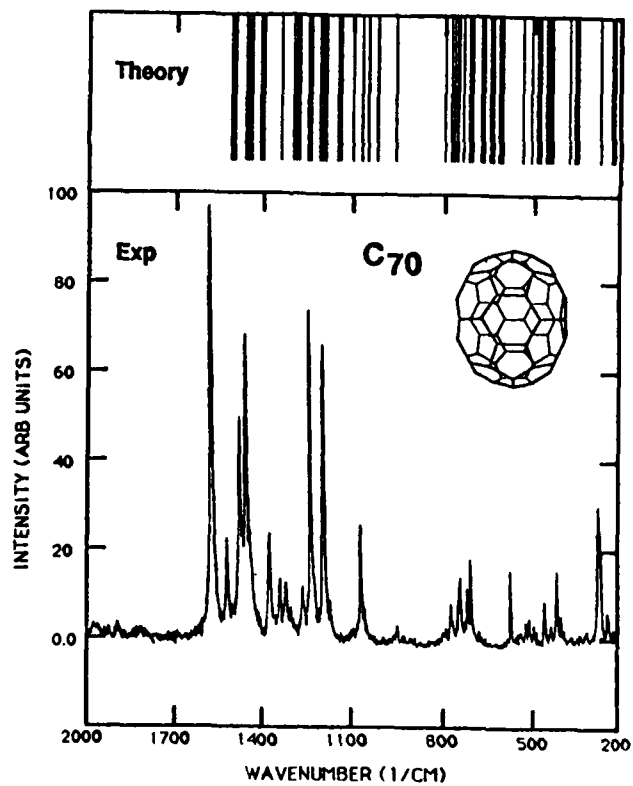
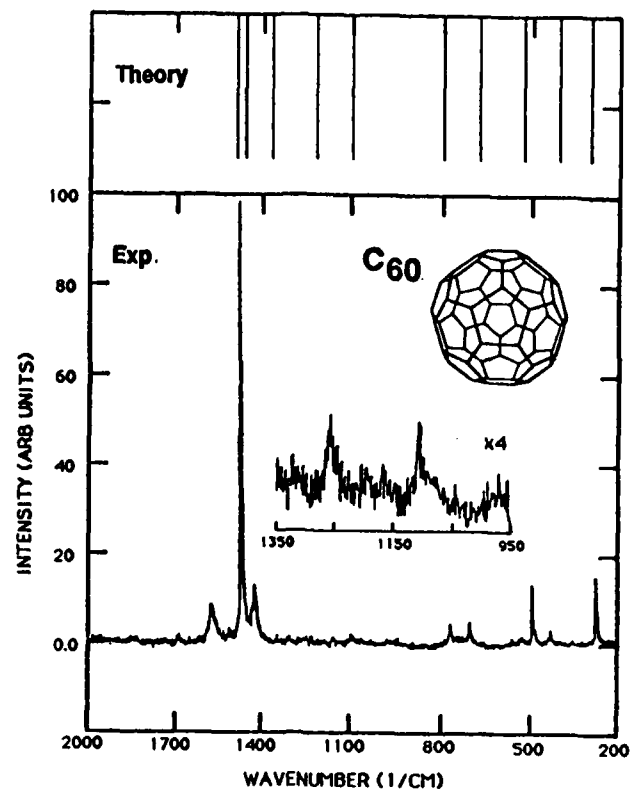


Figure 1

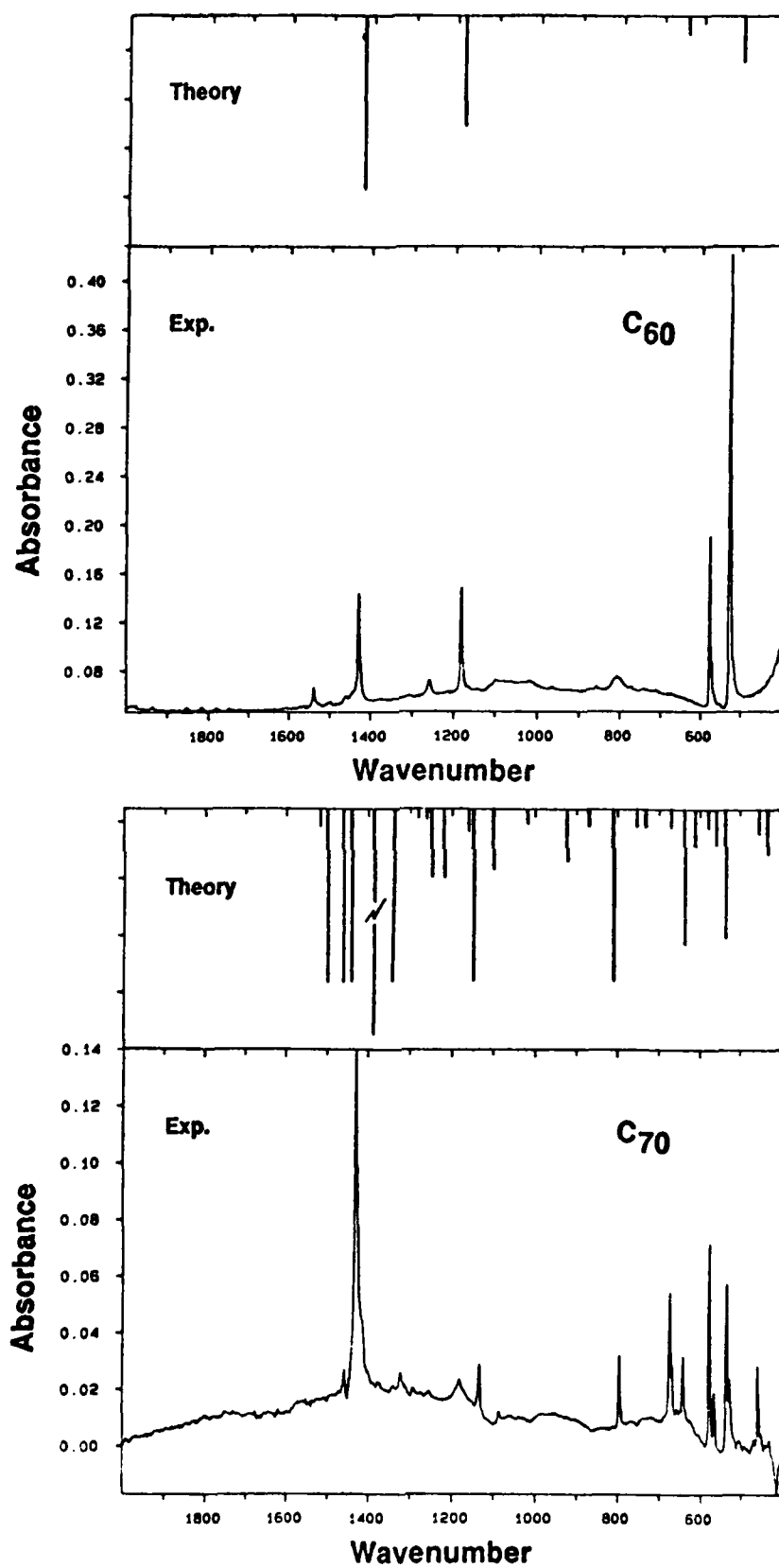


Figure 2

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